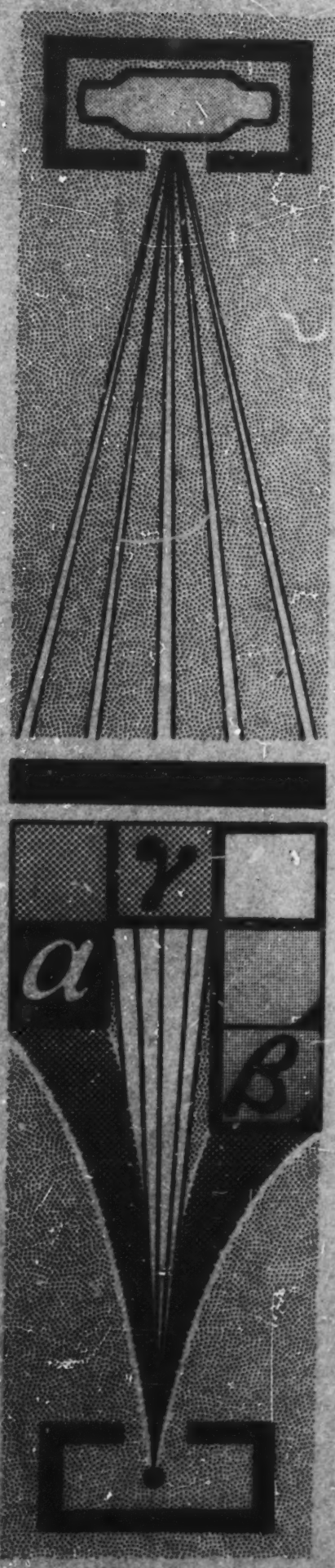

BRH/DMRE 70-5

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The USE of RADIOACTIVE MATERIALS in GAS CHROMATOGRAPHY

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service

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The USE of RADIOACTIVE MATERIALS in GAS CHROMATOGRAPHY

by

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OCTOBER 1970

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service

Bureau of Radiological Health
Rockville, Maryland 20852

FOREWORD

The Bureau of Radiological Health implements a national program designed to reduce the exposure of man to hazardous ionizing and nonionizing radiation.

Within the Bureau, the Division of Medical Radiation Exposure deals with 1) the reduction of unproductive ionizing radiation exposure of patients, workers, and others exposed by the use of x-rays and other machine-produced ionizing radiation, radioactive materials and radiopharmaceuticals, and 2) the improvement of radiological "systems" and methodology in the healing arts.

The Bureau publishes its findings in Radiological Health Data and Reports (a monthly publication), Public Health Service numbered reports, appropriate scientific journals, and technical report series for the Bureau's divisions, offices, and laboratories.

The technical reports of the Division of Medical Radiation Exposure allow comprehensive and rapid publishing of the results of intramural and contractor projects. The reports are distributed to State and local radiological health program personnel, Bureau technical staff, Bureau advisory committee members, university radiation safety officers, libraries and information services, industry, hospitals, laboratories, schools, the press, and other interested individuals. These reports are also included in the collections of the Library of Congress and the National Technical Information Service (formerly the Clearinghouse for Federal Scientific and Technical Information).

I encourage the readers of these reports to inform the Bureau of any omissions or errors. Your additional comments or requests for further information are also solicited.

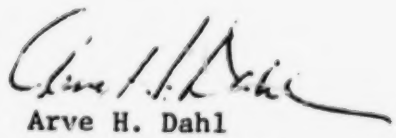
John C. Villforth
Director
Bureau of Radiological Health

PREFACE

The development and promulgation of information regarding reduction of radiation exposure from x rays, radioactive materials and the practice of nuclear medicine is the major responsibility of the Division of Medical Radiation Exposure, Bureau of Radiological Health.

It is the purpose of this report to familiarize the reader with: (1) operating principles of gas chromatography, (2) the hazards from radioactive materials used in chromatographs, and (3) safety precautions which could minimize the hazards.

It is hoped that such an approach will result in a safer utilization of this radiation source.



Arve H. Dahl
Acting Director
Division of Medical Radiation
Exposure

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THE USE OF RADIOACTIVE MATERIALS IN GAS CHROMATOGRAPHY

INTRODUCTION

The advent of chromatography in the early twentieth century greatly enhanced the capacity for analysis of organic compounds. Since that time, many different types of chromatography have been developed, all based on the same principle.

This document outlines the general principles of operation of gas chromatographs. Chromatograph detectors which utilize radionuclides are described in detail, together with their radiation hazards and some suggested precautions which should be taken.

Details relating to source type, radionuclide, and activity were compiled from information supplied by manufacturers and/or suppliers of gas chromatographs which use radioactive material. Of the 68 companies which were queried, only 15 indicated that they sold such devices.

GENERAL PRINCIPLE OF OPERATION

Gas chromatography is used in laboratories in hospitals, universities and industry, as a primary method for analyzing organic and inorganic compounds.

The basic components of the system shown in figure 1, are: inlet heater, column, column oven, detector cell, detector oven, and associated electronic circuitry to amplify and record the detector signal.

The sample mixture is introduced into the system at the sample injection port and is vaporized by the inlet heater. The vaporized sample is then "carried" through the system by an inert carrier gas which is continuously supplied through the gas port at a regulated flow rate.

The column is packed with particles of a porous, inert solid coated with a liquid phase material. This nonvolatile packing serves to selectively retard the various constituents of the sample. Because of the variation in adsorption characteristics, each chemical component of the sample emerges from the column into the detector cell at a different time. As each component is "carried" through the detector cell, a signal is produced, amplified, and recorded. The recorder plots the degree of detector response versus the time of emergence into the chamber.

Each chemical compound will exhibit a specific retention time for a particular column. Before analyzing an unknown sample, standard compounds are individually passed through the column to plot their retention curves. Then the unknown sample is passed through the column,

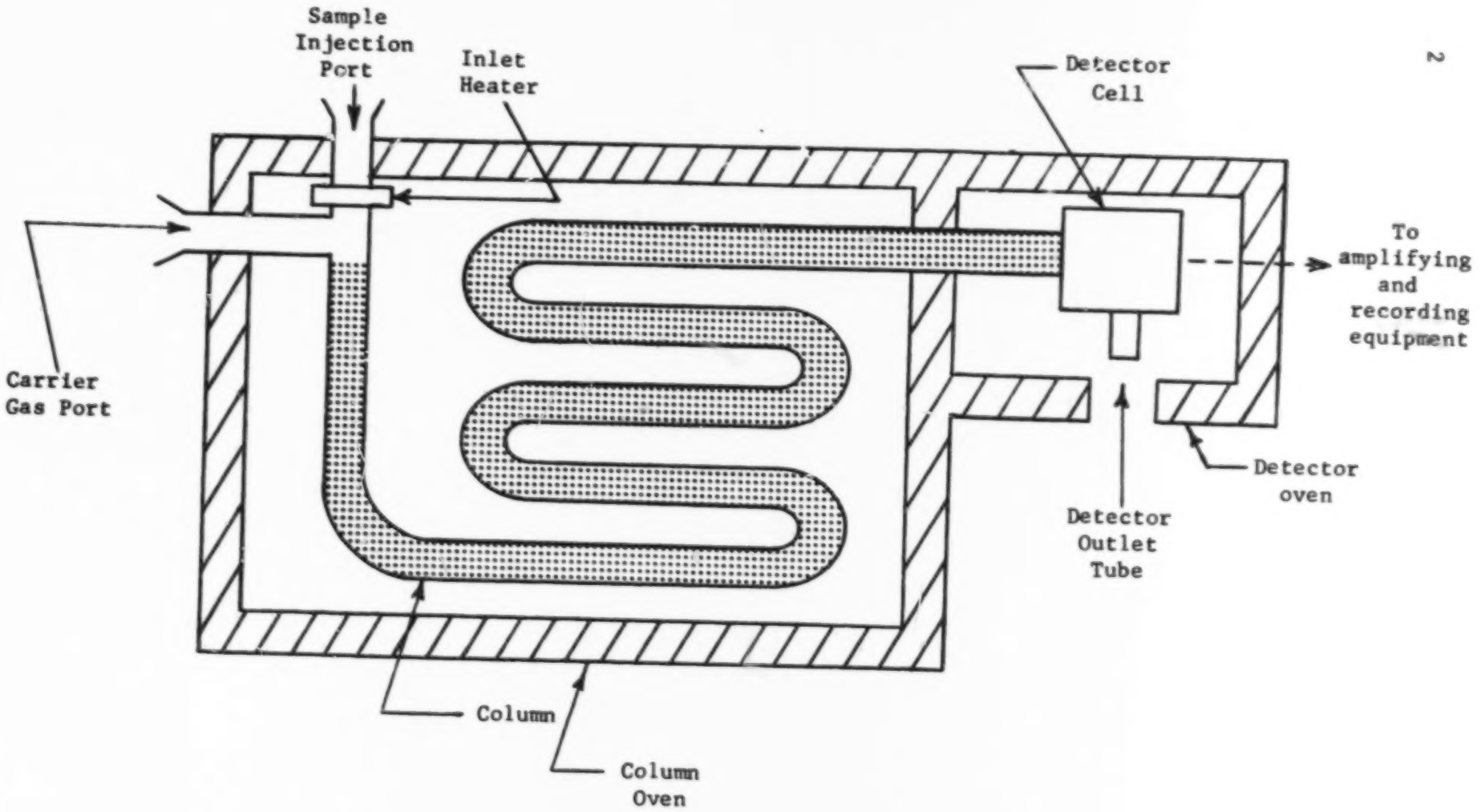


Figure 1. Schematic diagram of a gas chromatograph

and the resultant curves are recorded. These are compared with the curves produced by the standards to determine the unknown constituents of the sample. Figure 2 is a sample of such an analysis.

A quantitative analysis of each constituent of the sample can be achieved by analyzing the peak size at a specific retention time in a manner similar to that used in gamma spectrometry. The height or area of the sample peak can be related to the corresponding peak of the known standard to determine the amount of the material present in the sample.

DETECTION UNITS

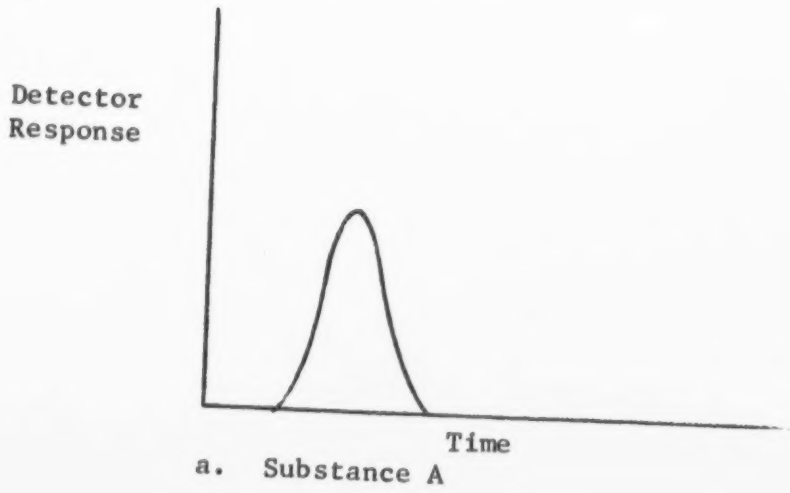
In any given chromatograph, the detector may be changed to suit the specific analytical purpose. Among the various detectors are: thermal, gas balance, biological, spectrometric, electron capture, and ionization. Radioactive sources are used only in the electron capture detector and in two types of ionization detectors, the argon ionization detector and the cross-section detector. The selection of the detector is dependent upon the type of compound under investigation.

The chromatograph manufacturers and/or suppliers reported 145 different detector models which use radionuclides. Of these models, 6 percent were argon ionization detectors, 52 percent were cross-section detectors, and 42 percent were electron capture detectors. The general principles of operation of these three detectors are as follows:

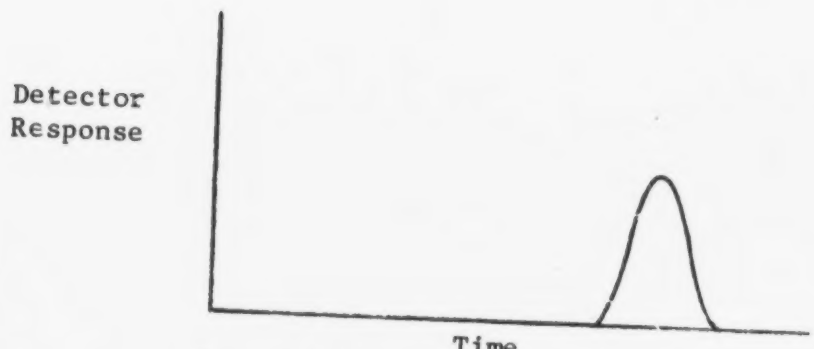
1. Argon Ionization Detector

Atoms of the argon carrier gas enter the detector cell where some are ionized by the alpha or beta particles from radium-226, radium-D, strontium-90, or tritium to yield electrons and positive argon ions. The primary electrons are accelerated across the detector by a potential difference great enough to excite large numbers of additional argon atoms to a metastable state. In noble gases, the metastable state is unusual in that the excited atoms have a life-time sufficient to allow the concentration of metastable atoms to approach that of the ions, under steady irradiation conditions.

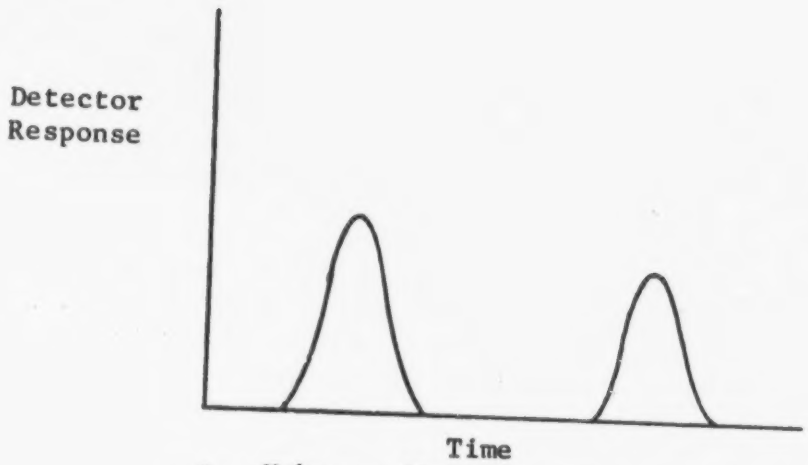
During analysis, the sample constituent, in vapor form, is carried by the argon gas into the cell containing the excited argon atoms. There collisions take place between the sample and the excited argon atoms. If the ionization potential of the sample molecules is less than the excitation potential of the argon atoms, energy is transferred during the collision process, causing ionization of the sample molecules. The excited argon then returns to ground state and secondary electron production occurs in the sample. The ionization current produced by these dlectrons, which is proportional to the concentration of the sample in the carrier gas, is then amplified and recorded.



a. Substance A



b. Substance B



c. Unknown displaying characteristic retention times of substances A and B

Figure 2. Chromatogram analysis

2. Cross-Section Detector

The cross-section detector consists of a detector cell connected to a voltage source with a means for measuring current across the cell. Hydrogen or helium is employed as the carrier gas. Strontium-90, tritium, or radium-226 is commonly used as the ion source in the detector cell. The ionization current is small when the cell contains only hydrogen or helium. Ionization current increases when the vaporized sample constituent is introduced into the cell, since the sample has more electrons per molecule than hydrogen and helium and thus more probability of being ionized.

The total molecular cross-section for ionization by a given radiation is simply the sum of the atomic cross-sections of the constituents of the molecule, for the same radiation. The molecular cross-section is almost completely independent of the nature of the chemical combination.

In practice, the potential applied to the cell is always sufficient to collect the ions without significant loss by recombination or other causes; the rate of ion production, therefore, is directly proportional to the observed current flow.

3. Electron Capture Detector

In electron capture detection, an effectively constant signal is provided by a pulsed field of beta particles, usually from a radium-226, tritium, strontium-90, or nickel-63 source. Neutral molecules of the sample, on passing through the detector cell containing the radiation source, can capture free electrons to form negative "molecule-ions." This effectively removes electrons from the system and substitutes negative ions of far greater mass. The negative ions combine with one of the many positive ions formed from the carrier gas, to be eluted as a neutral complex. The probability of an electron capture is dependent upon the electron affinity of the sample. As electrons are removed from the system, the corresponding drop in detector current is recorded, to enable measurement of the concentration of the sample vapor.

RADIOACTIVE SOURCES

As noted, the radionuclides most commonly used as ion sources in chromatographic detectors are radium-226, radium-D, strontium-90, nickel-63, and tritium. The strontium-90 sources, because of their energetic beta particles, are commonly used in the form of sealed sources with a thin stainless steel "window" to allow penetration of the beta particles. The other sources are usually in the form of foils, to reduce absorption of alpha or beta particles by the source encapsulation. Table 1 shows the percentage of reported detector models which use each radionuclide and the range of activities usually employed for that radionuclide.

Table 1. Distribution of radionuclides and activities in chromatograph detectors

Radionuclide	Percentage of reported detector models	Activity range (mCi)
Radium-D	0.7	.1
Radium-226	5.7	.05-.1
Tritium	80.0	100-300
Strontium-90	11.5	10-20
Nickel-63	2.1	2-15

The predominant radionuclide is tritium, used in 80% of the models reported. However, many of the models may employ several radionuclides interchangeably.

The activity of the source is selected to provide an ionization current of 10^{-7} to 10^{-9} amperes in the detector cell. The choice of radionuclide is a function of the sensitivity desired and the "noise level" (fluctuation in background current) which can be tolerated.

The fluctuation in ion current background depends on the statistical randomness of ion emission from the radiation source. A radiation source emitting alpha particles, which are highly ionizing, will produce much greater fluctuation in the collected ion current than one emitting particles which are less densely ionizing. Alpha radiation which generates 10^5 to 10^6 ion pairs per disintegration would be efficient for providing high current at a low radiation intensity, but the low activity required would result in an excessive noise level. Gamma radiation would produce fewer ion pairs, but an ion current of 10^{-7} amperes would require a prohibitively large radiation source. Beta radiation provides the best compromise between these extremes.

RADIATION HAZARDS AND PRECAUTIONS

Hazards from the radioactive materials used in the detectors fall into two categories, external and internal radiation exposure. The degree of hazard is dependent upon the radionuclide used, the activity and encapsulation, and the operating factors involving the use of the source.

1. External Radiation

External radiation from tritium, nickel-63, and radium-D is generally absorbed within the detector itself. Detectors containing strontium-90 and radium-226 sources usually contain shielding material built into the chromatograph or detector cell to reduce the gamma, beta, and any associated bremsstrahlung radiation. Limited data supplied by manufacturers indicated that exposure rates at the surface of the cabinets, for

chromatographs with detectors containing radium-226, were less than 2 mR/hr for a 56 μCi source. For the same source the exposure rate at one inch from the surface of the detector cell was 8-10 mR/hr. This may increase to 20-25 mR/hr. when the anode end of the detector cell is open. While the exposure rate at the cabinet surface for strontium-90 sources is comparable to that from the radium-226 sources, the external field at the surface of a detector cell containing a 20 mCi strontium-90 source is on the order of 25-40 mR/hr. Because of direct beta emission, the exposure rate from the strontium-90 source at the open anode end may be 80 times as great as its side measurements. Therefore, proper procedures should be followed for handling of these sources during maintenance and repair, to minimize exposure to individuals, especially extremity exposure.

2. Internal Radiation

Internal hazards arise when radioactive material is liberated from the source. This may occur as a result of (a) mechanical damage to the source during cleaning or handling, (b) emission of radioactive gas such as radon or tritium (from dissociation of titanium tritide), (c) chemical attack on the source by the material being investigated or by a corrosive cleaning solvent, and (d) damage to the source from excessive heat. To reduce the possibility of internal exposure of individuals, the following precautions should be followed.

a. Operating temperatures

Operating temperatures of detectors employing radioactive sources range from approximately 200°C.to above 450°C. Licenses for the use of detectors containing tritium specify a maximum operating temperature of 225°C, to prevent dissociation of the titanium tritide in the source and consequent evolution of tritium gas. Normally, operating temperatures are well below this limit. Detectors containing sealed sources such as strontium-90 may be operated at a much higher temperature, since heat damage is less likely. Equipping chromatographs with temperature controls, and labeling detector cells as to maximum operating temperatures, can help prevent accidental overheating of the source. This is especially critical in chromatographs which employ tritium sources.

b. Cleaning

Cleaning the detector and sources is occassionally necessary to remove deposits of organic substances which impair the operation of the detector by reducing its sensitivity. Several manufacturers suggest that the detector be returned to them for periodic maintenance and cleaning. Others provide instructions for the user to clean the detector. Strontium-90 sources are frequently cleaned in place by introducing a solvent into the system or by operating the detector at a higher temperature to bake off residues. Ultrasonic cleaning is used for many detector parts, particularly radiation sources which cannot be subjected to elevated temperatures. Tritium foils lose some activity during

ultrasonic cleaning by mechanical removal of small amounts of titanium tritide from the foil backing. The cleaning solvent thus becomes contaminated and must be disposed of in accordance with applicable regulations. The users of tritium detectors should be aware of this hazard and should have a standard procedure for cleaning the detector, decontaminating the ultrasonic cleaner, and disposing of the waste liquid.

c. Storage

Many chromatograph users have several detector cells available for use with each unit. Care must be exercised to insure that each detector cell is properly labeled and that it is stored in a location secured from fire or theft.

d. Labeling

All detector cells containing radiation sources used under an AEC or State license must be labeled with the radiation symbol, the words "Caution-Radioactive Materials," and the type and activity of the source. It is also desirable to add the date on which the activity was measured. The elevated operating temperature of detector cells frequently causes labels of the traditional radiation warning colors, magenta on yellow, to fade rapidly. Consequently, the AEC and the Agreement States have granted an exemption to the color requirement for many of the labels used for this purpose. When detector cells containing radioactive materials are being utilized, a warning label should also be posted on the chromatograph.

e. Ventilation

Vapor emissions from the chromatograph should be vented to a fume hood or to the outside environment, not to the laboratory atmosphere. Such venting will protect laboratory personnel from exposure to radioactive materials in the event of heat damage or chemical attack on the source.

f. Handling

Physical handling of the sources should be minimized. If handling is necessary, rubber or plastic tipped tongs or forceps should be used to prevent abrasive damage to the source and/or possible contamination of the hands.

g. Leak Testing

Because of the numerous possibilities for liberation of the radioactive material, strontium-90 and radium-226 sources are usually required by regulatory agencies to be leak tested at 6-month intervals. As the radium source is in the form of a thin foil, radon daughters may be found from a

leak test, especially a wipe test. This should be taken into consideration when determining the leak test method (e.g., counting of a wipe may be delayed until any short-lived contamination has decayed away).

CONTROL OVER CHROMATOGRAPHS

All chromatographic detectors which contain by-product materials are controlled through licensure by the AEC or the Agreement States. Several types of detector, especially those using tritium, may now be used under a general license.

Although radium is not within the jurisdiction of the AEC, detectors containing radium are required to be licensed or registered in most States. However, non-Agreement States have limited control over manufacturers and/or distributors and the State radiological health agencies often have difficulty locating users in such States. Also, users are often unaware that they may be required to comply with certain regulations. Table 2 lists known manufacturers of chromatographs which use radium and identifies the type of detector, as well as the activity and size of the radium source.

Table 2. Chromatographs using radium-226 or radium-D

Manufacturer	Detector		Source[a]			Chromatograph model nos.
	Type[b]	Model nos.	Model nos.	Activity (μCi)	Size (inches)	
Advanced Technology Inc.[c] 1830 York Road Timonium, Md.	E.C.	None	Lab-204	56	2.5 x 5/8 x .007	Au-8 and Cu-4
Barber-Coleman Co. 55 Clifford Ave. Rockford, Illinois	C.S.	A4071	Lab-204	56	2.2 x 5/8 x .007	Models 10,15,20,5360 and Series 5000
	"	A4072	"	"	"	"
	"	A4146	"	"	"	"
	"	A4149	"	"	"	"
	"	A4183	"	88	1.2 x .4 x .007	"
	"	A4765	"	"	"	61C
Packard Instrument Co., Inc. 220 Warrenville Rd. Downers Grove, Ill.	A.I.	810	Lab-204-1	d_{50}	1.5 x 1.5 x .002	
Glowall Corporation Easton & Dansville Rd. Willow Grove, Pa.		AD225	T-75	22.5		110,210,310,320 330, and 400

[a] All sources manufactured by U.S. Radium Corp.
[b] E.C. - Electron Capture; C.S. - Cross Section; A.I. - Argon Ionization.
[c] Formerly Electronic Communications, Inc. and Electronic Instruments for Research.
[d] This source is radium-D; all others listed are radium-226.

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The use of radioactive materials in gas chromatography.
Accession No.
U.S. Department of Health, Education, and Welfare, Public Health Service Publication Number BRH/DMRE 70-5. (October 1970) 11 pp. (limited distribution).

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